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Low-Field NMR Analyses of Gels and Starch-Stabilized Emulsions with Modified Potato Starches

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Abstract: Many different biopolymers are used to stabilize emulsions, of which starch is of particular concern. To improve the characteristics and technical utility of native starch, various types of changes can be made. This article is a report describing the molecular dynamics of water by the low-field nuclear magnetic resonance (LF NMR) of chemically (E 1412 and E 1420) and physically modified starch (LU 1432) gels and the effect of their use on the stability of oil/water emulsions obtained using bovine and porcine fats. The analysis of changes in spin–spin and spin–lattice relaxation times over time showed that the presence of the type of starch modification significantly affects the values of T_1 and T_2 relaxation times, as well as the correlation times. Research on time-related changes in water binding in oil-in-water emulsions showed that potato starch modified by chemical methods can be used as an emulsifier. Compared to physically modified starch, chemically modified starches have a much better water-binding capacity.

Keywords: relaxation time; oil-in-water emulsion; water binding; molecular dynamics; water behavior; relaxometry



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1. Introduction

Starch, one of the two most abundant biopolymers in nature, is produced by many plants as an energy storage compound. It consists of two fractions—linear amylose composed of anhydroglucose units linked by α -1,4-glycosidic bonds and branched amylopectin containing additional α -1,6-glycosidic bonds [1,2].

Natural starch, although widely used in many areas of life for years, has some disadvantages that affect its functionality. The main disadvantage of native starch is the instability of the paste it creates [3]. The viscosity of the starch solution may change under the influence of temperature, mechanical forces (mixing), changes in the reaction of the environment, and pressure. Clear starch solutions, after cooling down and forming a gel, quickly retrograde, which is externally evident by the clouding of the paste [4,5]. Various modifications are used to eliminate these drawbacks. They are intended to improve certain functional properties or to impart new properties, specific to a given application. On the industrial scale, starches are modified with physical, chemical, and enzymatic methods or combinations of these [6–8].

Modifications of starch are aimed at giving it new physicochemical and functional properties not present in native starches. As a result of these modifications, the obtained modified starches differ significantly from natural starches in at least one property. This mainly applies to rheological properties [9,10] such as the binding of large amounts of water with substances dissolved in it; viscosity; gelatinization temperature; formation of various types of gels; not yielding to or being slightly retrograde; clarity and transparency of pastes and gels; absorption of various compounds; or the ability to emulsify lipophilic compounds in water and to stabilize emulsions and suspensions.

Starch is widely used in many industries, whether it serves as a filler, binder, or glue [11–14]. In the food industry, native starch is often used as a thickening agent or stabilizer. In addition, it has also found wide application in the production technologies of meat preparations, especially as a good substitute for fats in low-calorie products [15].

The growing demand for low-fat meat products prompts producers to modify their existing recipes. Starch is frequently used to partially substitute fat in meat products [16]. In the presence of a sufficiently large amount of water and during heating, the starch granules lose their native structure, and the system takes the form of a sol. As the starch system cools in the water, the gelatinization process takes place [17]. Therefore, it seems interesting to understand the mechanisms of the interaction of animal fat and starch during the gelatinization process.

In the 1990s, low-field nuclear magnetic resonance became a method for studying many biological systems [18–20], such as food or model biopolymers [21–25]. In contrast to other analytical methods of biopolymer gel characterization, LF NMR is a technique that does not destroy the samples analyzed, and therefore it is possible to perform multiple measurements on the same system, e.g., examine the retrogradation processes or changes in water behavior during storage [26]. The tests consist in measuring spin–lattice T_1 relaxation times or spin–spin T_2 relaxation times or the analysis of the free induction decay shape [26,27]. Due to the use of magnetic fields, the induction value of which (B_0) does not exceed 1 Tesla, this method is very well suited for studying the interactions between water molecules and other macromolecules in the system. It is therefore a good method of analyzing biopolymer gels. The LF NMR method enables the analysis of the molecular dynamics of water, which is a solvent, i.e., the liquid phase of a biopolymer gel [28,29]. The processes of proton relaxation in such systems are, compared to the state of liquid water, slowed down due to the presence of biomolecules forming a spatial lattice. The use of this method complements the knowledge of biopolymer systems at the molecular level. A detailed analysis of changes in the molecular dynamics of water in biopolymer gels may also be an important contribution to understanding the issues of starch retrogradation at the molecular level [30].

Considering the above, research was undertaken to track changes in the molecular dynamics of protons in the systems of oil-in-water (O/W)-type emulsions and to analyze the impact of the presence of potato starch modified with various methods (physically and chemically) on the stability of such systems.

2. Materials and Methods

2.1. Materials

The tested materials were two chemically modified potato starches (E 1420 and E 1412) and one physically modified (LU 1432). Ready, commercial modified starches were purchased from WPPZ S.A. (Luboń, Poland). Fats (bovine and porcine) were obtained from Animex Foods sp. z o.o. (Morliny, Poland).

2.2. Preparation of Gels

The prepared starch suspensions in water (0.25 g/g) were subjected to thermal treatment (90 °C) in a water bath for 1 h with constant stirring. The obtained starch gels were then placed in glass tubes and sealed using Parafilm®. LF NMR measurements were taken for 8 h at 1 h intervals. Between the measurements, the samples were stored in a refrigerator (4 °C), and before the next measurements, the samples were heated in the spectrometer head to the measurement temperature (25 °C).

2.3. Preparation of Emulsions

O/W emulsions were prepared according to the method described earlier by Małyszek et al. [31]. Emulsions containing 1 part starch, 1 part fat, and 3 parts water were analyzed. Briefly, the tested fats and water, before mixing with starch, were heated to a temperature of 40 °C, and then, after adding starch, the sample was heated to 90 °C and thermostated

for 1 h with continuous stirring using a mechanical stirrer MS-H-Pro (ChemLab, Kielce, Poland) at 300 rpm. Freshly prepared samples were placed in NMR tubes, sealed with Parafilm[®], and placed in an NMR spectrometer.

2.4. ¹H NMR Relaxometry

Measurements of spin–lattice T_1 and spin–spin T_2 relaxation times were carried out using a pulsed NMR spectrometer (Ellab, Poznań, Poland) equipped with an integral temperature control system. The device was operating at a frequency of 15 MHz at the temperature of $25.0\text{ }^\circ\text{C} \pm 0.5\text{ }^\circ\text{C}$. For T_1 measurements, the inversion–recovery pulse sequence (π – TI – $\pi/2$) was used [27], and the distances between pulses (TI) were varied from 2 to 2000 ms. Each time, 32 sequences of pulses were generated, and 119 points were collected on each signal of free induction decay (FID) recorded after the $\pi/2$ pulse. The repetition time between successive pulse sequences was 15 s. The values of T_1 were calculated with the use of the CracSpin program [32], in which the Marquardt method enables minimization by fitting to the multi-exponential course of the magnetization regrowth curve. The regrowth of the longitudinal component of magnetization (M_z) is described by the formula (Equation (1)):

$$M_z = M_0 \sum_{i=1}^n p_i \left[1 - 2 \exp\left(\frac{-TI}{T_{1i}}\right) \right] \quad (1)$$

where M_0 —equilibrium value of magnetization, p_i —fraction of protons relaxing with time T_{1i} .

For T_2 measurements, a CPMG impulse sequence ($\pi/2$ – TE – π_n) was used [33,34]. The distance between the spin echoes ($2TE$) was 3 ms. The 5 accumulation signals were applied in a spin echo sequence. The decay of the spin echo amplitudes ($M_{x,y}$) can be expressed by the formula (Equation (2)):

$$M_{x,y} = M_0 \sum_{i=1}^n p_i e^{-\frac{TE}{T_{2i}}} \quad (2)$$

where p_i —fraction of protons relaxing with time T_{2i} .

The calculation of the relaxation time was performed with the adjustment of the recorded delays of the spin echo amplitudes to the formula taking into account the multi-exponential delay.

The relaxation time values were used to calculate the correlation times (τ_c), in accordance with Bloembergen–Purcell–Pound formulas [35] (Equations (2) and (3)):

$$R_1 = \frac{1}{T_1} = \frac{6}{20} \frac{\mu_0^2}{16\pi^2} \frac{\gamma^4 \left(\frac{h}{2\pi}\right)^2}{r_0^6} \left[\frac{\tau_c}{1 + (\omega\tau_c)^2} + \frac{4\tau_c}{1 + (2\omega\tau_c)^2} \right] \quad (3)$$

$$R_2 = \frac{1}{T_2} = \frac{3}{20} \frac{\mu_0^2}{16\pi^2} \frac{\gamma^4 \left(\frac{h}{2\pi}\right)^2}{r_0^6} \left[3\tau_c + \frac{5\tau_c}{1 + (\omega\tau_c)^2} + \frac{2\tau_c}{1 + (2\omega\tau_c)^2} \right] \quad (4)$$

where μ_0 is the permittivity of free space, γ is the magnetogyric ratio, h is the Planck constant, r_0 is the distance of the interacting nuclei, and ω is the resonance frequency ($\omega = 2\pi f$, f is the Larmor frequency, the spectrometer frequency).

3. Results and Discussion

3.1. Relaxation of Starch Gels

In the first step, the molecular dynamics of water in modified starch gels were analyzed. The time value T_1 corresponds to the bulk water content, while the value T_2 describes the mobility of water molecules [26,27]. The starch concentration was constant and amounted to 0.25 g/g in each sample. All gels had one spin–lattice (T_1) relaxation time and one

spin–spin (T_2) relaxation time (Table 1). This reflects a rapid chemical energy exchange between the protons of the molecules of water hydrating the biopolymer and the molecules of water located in the spaces in the polymer network [36].

Table 1. Values of spin–lattice (T_1) and spin–spin (T_2) relaxation times in modified potato starch gels.

Time (h)	E 1420		E 1412		LU 1432	
	T_1 (ms)	T_2 (ms)	T_1 (ms)	T_2 (ms)	T_1 (ms)	T_2 (ms)
0	573	244	451	193	451	201
1	564	255	465	215	461	221
2	558	276	477	200	453	220
3	560	245	478	201	453	215
4	558	250	468	200	451	200
5	559	238	480	196	453	210
6	553	228	473	180	449	246
7	561	241	472	203	451	203
8	558	229	480	202	460	202

Changes in the values of the correlation times in the starch gels tested over time are shown in Figure 1. This parameter characterizes the rotational movement of molecules containing protons; thus, it describes the freedom of molecular movement in the analyzed samples [37]. In the gels of chemically modified starch, a significant increase in the values of the correlation times is observed up to about 3 h from the moment the gel reaches the ambient temperature; then, the values of τ_c decrease. A similar course of τ_c was recorded for native starch gels [38]. This means that water is first bound in the structure of the starch gel, and then it is removed inside the network. The recorded lower values of mean correlation times for E 1420 starch gels, compared to E 1412, mean that the water in this system is bound less strongly. All analyzed starches are characterized by changes in the values of mean correlation times in the time interval from about 1 to 6 h; however, it was found that these changes were much smaller in the case of LU 1432 starch gels. It can therefore be concluded that the physically modified potato starch forms gels with a structure more stable over time, and the changes in water binding in such gels are small, which was also demonstrated in the studies described by Małyszczek et al. [31].

3.2. Relaxation of O/W Emulsions

In order to prepare a stable emulsion, it is necessary to use an additional substance that reduces the interfacial tension at the oil/water interface. Reducing the fat content in the absence of technological additives results in free water in the system [39]. For this reason, in order to obtain a stable emulsion with a reduced fat content, it is necessary to use emulsifying substances. Starch does not have the ability to do this; nevertheless, it acts as an emulsion stabilizer, effectively increasing the stability of the two-phase system [40]. Emulsifiers are substances that promote the formation of emulsions and stabilize them for a short time due to interfacial interaction. On the other hand, the role of emulsion stabilizers is attributed to polysaccharides or, more broadly, to hydrocolloids, mainly through the mechanism of increasing the viscosity of the dispersion phase. Long-term stability of the emulsion is thus provided, possibly due to the adsorption mechanism [40–42]. Native starch can also be used as an emulsion stabilizer, but it is not the most effective in this role. This is related to surface activity, which is much better in both physically and chemically modified starches. Modifications may improve the emulsifying capacity of starch, an example being OSA starch (E 1450) [43].

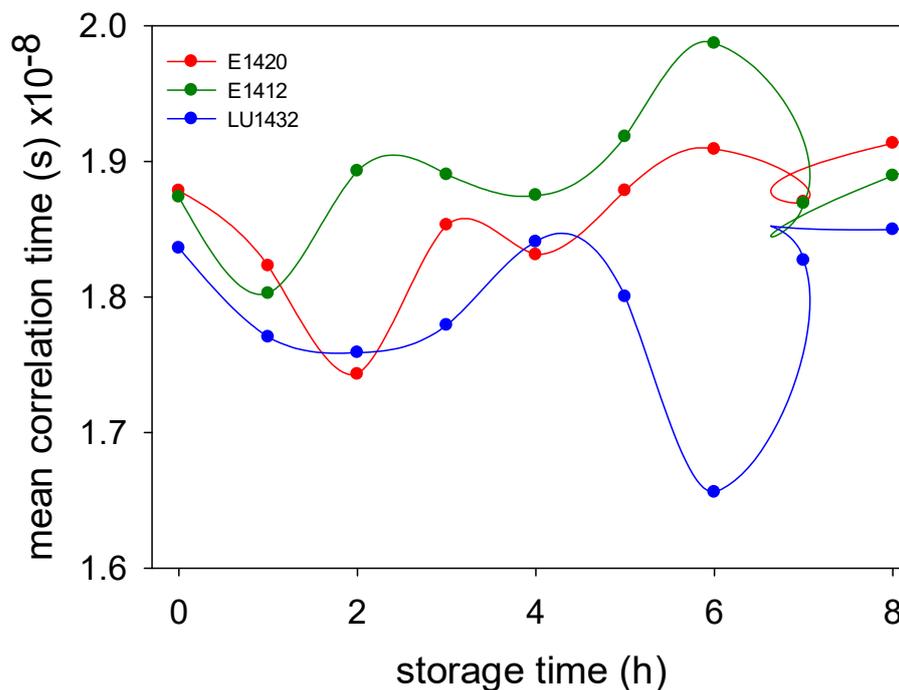


Figure 1. Time-related changes in values of correlation times in potato starch gels.

The changes in water binding in O/W emulsions stabilized with modified potato starches were analyzed up to 8 h. All emulsions contained three parts water, one part fat, and one part starch, so the starch concentration was always 0.25 g/g. The results of the relaxation times measurements are shown in Table 2. As in the case of O/W emulsions emulsified with native starch [38], two proton fractions were found in the emulsions emulsified with modified starches. Analyses of O/W emulsions with the addition of starch revealed two components of spin–lattice T_1 and spin–spin T_2 relaxation times, in line with published data [38]. This means that there were two proton fractions relaxing at different rates in the system and that the energy exchange between these proton fractions was much slower than the relaxation time [44]. The analysis of the values of both relaxation time components indicates that the long components (T_{12} and T_{22}) reflected the relaxation processes of proton fractions associated mainly with the biopolymer gel, and the short components of the relaxation times (T_{11} and T_{21}) were characterized by much lower values, which suggests that these components describe relaxation of the proton fraction of the fat emulsion. Therefore, the changes in long and short components of relaxation times in the studied emulsions were analyzed separately.

The time-related changes in the mean values of the correlation times of the mobility of water molecules were determined on the basis of the values of the relaxation times and are shown in Figure 2A–C. Porcine fat emulsions are characterized by longer correlation times, which means less inhibition of proton mobility. The fat fractions of protons in emulsions show temporary changes in values, but these changes, although significant over time, show a return to the initial values after 8 h. The protons of the starch fractions show a constant tendency to increase in value. Protons of fat fractions in emulsions with E 1412 starch show significantly longer values of correlation times, which means greater mobility of water molecules. Time-related changes occur to about 5 h for porcine fat. With the use of bovine fat, the system is stable after about 3 h. The protons of the starch fractions show a monotonic increase in value over time, indicating an increase in the mobility of water. The obtained results show that E 1420 and E 1412 starches show similar emulsifying properties due to the water-binding properties.

Table 2. Values of spin–lattice T_1 and spin–spin T_2 relaxation times in O/W emulsions emulsified with modified potato starches.

E 1420								
Time (h)	Porcine Fat				Bovine Fat			
	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)
0	44	33	657	270	64	31	653	313
1	57	28	650	271	57	37	637	272
2	81	30	667	254	61	34	636	266
3	40	22	638	217	44	35	632	250
4	61	27	654	213	68	34	634	255
5	52	20	635	205	87	35	634	249
6	65	27	645	193	47	33	629	210
7	76	26	641	200	60	34	634	228
8	52	28	633	177	95	37	632	211
E 1412								
Time (h)	Porcine Fat				Bovine Fat			
	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)
0	101	24	553	290	58	49	508	192
1	72	40	585	209	69	39	476	173
2	65	36	586	190	51	33	489	155
3	52	33	567	182	46	39	509	159
4	82	41	583	178	46	39	484	166
5	71	31	570	190	45	39	487	160
6	80	39	582	185	45	39	489	157
7	65	33	573	170	50	43	503	157
8	57	30	540	168	49	44	505	156
LU 1432								
Time (h)	Porcine Fat				Bovine Fat			
	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)
0	37	30	439	371	48	39	440	147
1	85	30	402	389	40	30	427	122
2	90	28	398	129	52	40	432	127
3	80	35	402	384	55	31	427	133
4	80	33	414	397	58	36	425	147
5	77	30	401	399	76	32	421	186
6	73	26	404	285	55	34	422	152
7	68	31	405	203	29	35	428	100
8	67	26	396	207	34	37	431	107

Literature data confirm that physically modified starch, despite its low surface activity, can be successfully used to create an O/W emulsion [45]. In the emulsions emulsified with starch LU 1432, changes were found depending on the applied fat. In the case of porcine fat, the fraction of fatty protons is less mobile than the fraction of starch protons. The opposite relationship was observed for bovine fat, where the fraction of fatty protons is definitely more mobile than the starch fraction.

Measurements of water binding in gels and O/W emulsions were also carried out in long-term storage. The tests were carried out up to 6 days from the moment of preparation of the emulsion, and the emulsions were stored at a temperature of 4 °C in the intervals between measurements. The values of relaxation times for starch gels are summarized in Table 3.

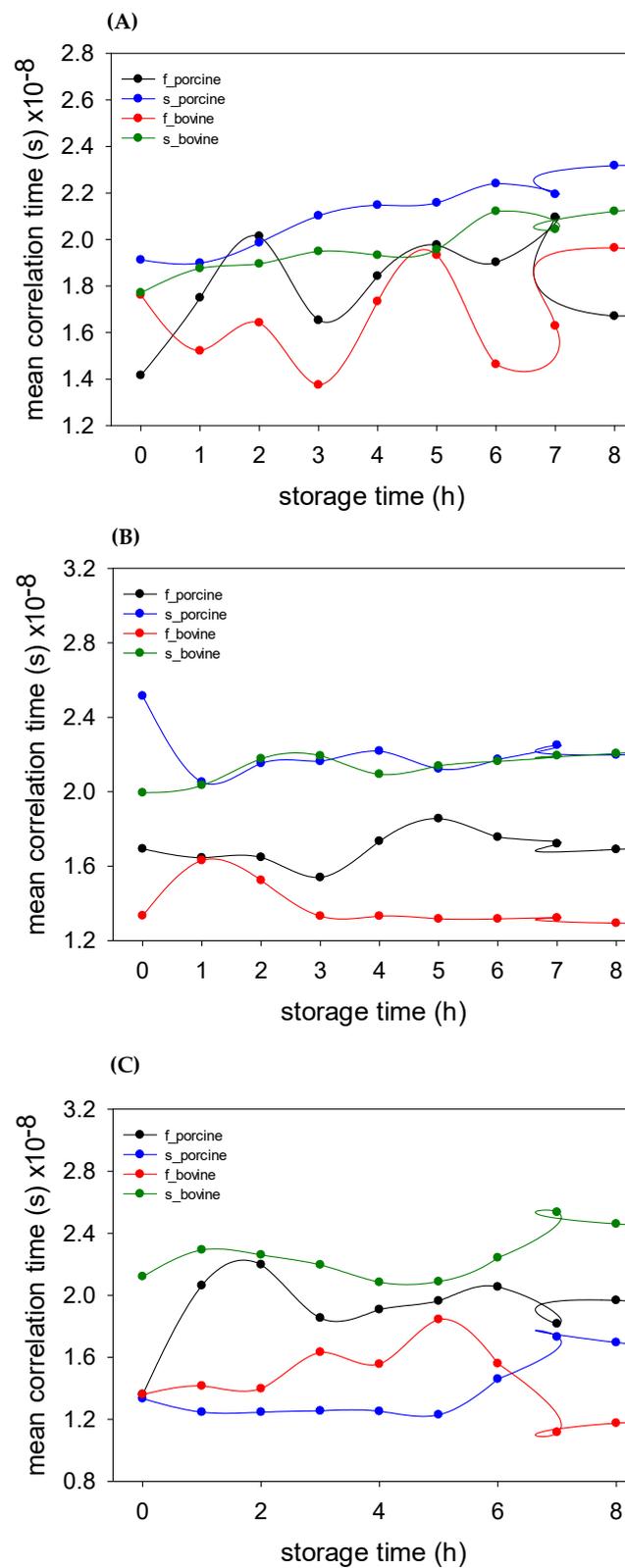


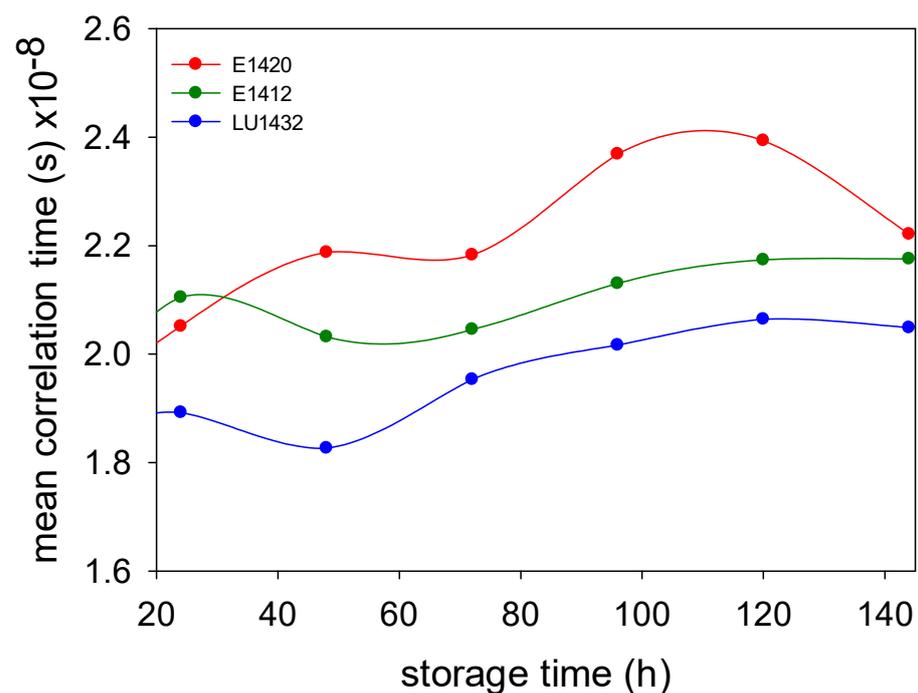
Figure 2. Time-related changes in the values of mean correlation times in O/W emulsions emulsified with (A) E 1420, (B) E 1412, and (C) LU 1432 starches. “f” and “s” denote the fat fraction and the starch fraction of the protons, respectively.

Table 3. Values of spin–lattice T_1 and spin–spin T_2 relaxation times in modified potato starch gels.

Time (h)	E 1420		E 1412		LU 1432	
	T_1 (ms)	T_2 (ms)	T_1 (ms)	T_2 (ms)	T_1 (ms)	T_2 (ms)
8	558	229	480	202	460	202
24	521	186	460	156	479	201
48	532	167	445	162	444	200
72	463	146	440	158	452	178
96	508	136	438	145	479	177
120	511	134	434	138	468	165
144	486	148	441	140	461	165

The values of relaxation times presented in the table indicate differences in T_1 values. The gels of unmodified potato starch (see [38]) and E 1421 starch show longer spin–lattice relaxation times than the E 1412 and LU 1432 starch gels, which suggests that E 1412 and LU 1432 bind water better. Such properties of starch gels may positively affect the long-term stability of food products in which these starches are used, suggesting their beneficial properties as food additives [46].

The changes in water binding of modified starches were analyzed by changes in the mean values of proton motion correlation times in the tested gels, and the obtained results are presented in Figure 3.

**Figure 3.** Long-term changes in mean values of proton motion correlation times in potato starch gels.

The obtained results show that LU 1432 starch gels are characterized by the shortest mean values of proton motion correlation times, which means that this starch binds water the least. On the other hand, E 1420 starch forms a gel with the strongest binding of water, which was also proven by other authors [47]. Gels made of modified starches E 1412 and LU 1432 show minimum τ_c values after about 2 days, which proves the initial release of water molecules by the network. After this time, an increase in the value of correlation times means a slow binding of water molecules outside the polymer network. Time-dependent changes in the relaxation times of the protons of starch and fat fractions in O/W emulsions emulsified with modified starches are summarized in Table 4.

Table 4. Values of spin–network T_1 and spin–spin T_2 relaxation time components in O/W emulsions emulsified with modified potato starches.

E 1429								
Time (h)	Porcine Fat				Bovine Fat			
	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)
8	52	28	633	177	95	30	632	211
24	71	29	636	175	66	36	601	167
48	54	37	637	148	70	33	599	165
72	74	50	653	165	72	40	593	169
96	68	42	621	140	89	50	602	175
120	75	42	623	163	66	48	596	180
144	64	36	600	155	44	27	594	190
E 1412								
Time (h)	Porcine Fat				Bovine Fat			
	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)
8	57	30	540	168	49	44	505	156
24	76	30	531	148	46	40	480	129
48	71	19	536	187	64	38	467	148
72	41	18	520	103	54	34	458	111
96	43	21	530	109	61	27	417	119
120	37	19	518	96	58	35	422	110
144	38	20	516	99	54	42	445	103
LU 1432								
Time (h)	Porcine Fat				Bovine Fat			
	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)	T_{11} (ms)	T_{21} (ms)	T_{12} (ms)	T_{22} (ms)
8	67	26	396	207	44	37	431	107
24	61	38	457	411	41	37	410	109
48	52	31	387	304	36	32	409	90
72	40	36	383	259	34	28	375	133
96	39	33	370	290	35	26	378	150
120	37	23	362	302	33	24	375	361
144	38	24	360	304	32	29	375	298

Based on the results of the relaxation times, the mean correlation times of protons in these fractions were calculated. Time-dependent changes in the values of correlation times allowed us to conclude about water binding in these systems. Fat proton fractions (T_{11} and T_{21}) in porcine and bovine fat emulsions are shown in Figures 4 and 5. In porcine fat emulsions, changes in the dynamics of water molecules are observed for up to 6 days, with the greatest changes being noted on days 2 to 4. After this time, however, all tested emulsions show similar correlation times.

In emulsions based on bovine fat, time-related changes in the molecular dynamics of the fat fraction show large differences due to the starch used in the emulsion. The lowest values of correlation times were found in the systems emulsified with LU 1432 starch. In comparison to emulsions with porcine fat, differences in the values of correlation times after 6 days of storage were found in emulsions with bovine fat.

Figures 6 and 7 show the time-dependent changes in the mean correlation times in the starch proton fractions (T_{12} and T_{22}) of the emulsion.

The use of LU 1432 starch as an emulsifier made the starch fraction of protons in the porcine fat emulsion stable in time. The mean values of proton motion correlation times are the smallest, which reflects the weakest binding of water compared to the other analyzed starches. The emulsions with E 1420 starch are also time-stable, but in this system, the correlation times are much longer compared to the LU 1432 starch-stabilized emulsions. This means that E 1420 starch is an emulsifier that inhibits molecular movements of protons

in the starch fraction of the emulsion. The best water binding, already after about 3 days of storage, was found when using starch E 1412 as an emulsifier in porcine fat emulsions.

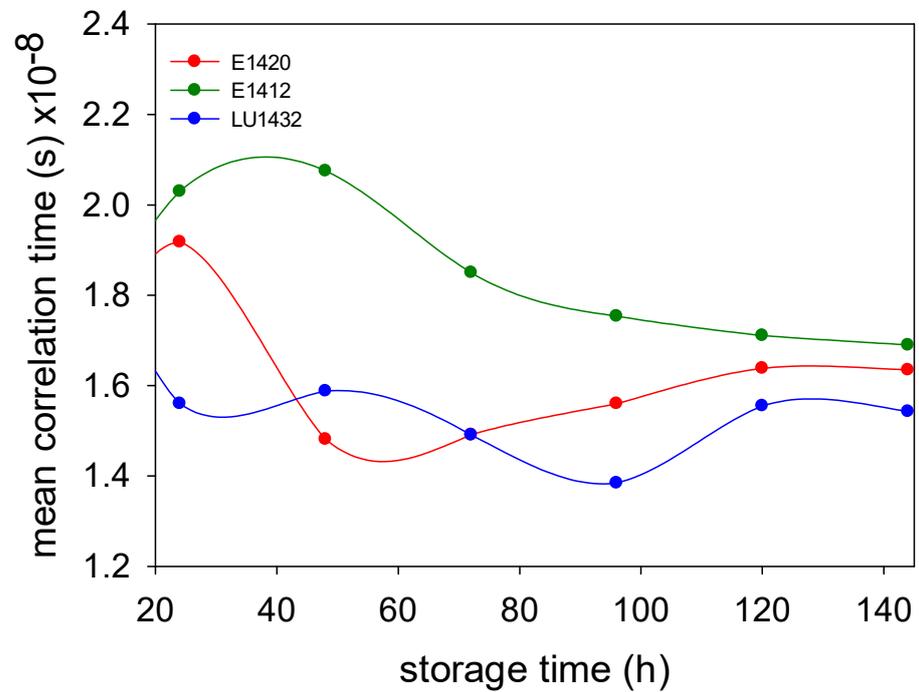


Figure 4. Time-dependent changes in mean values of proton motion correlation times of fat proton fraction in porcine fat emulsions.

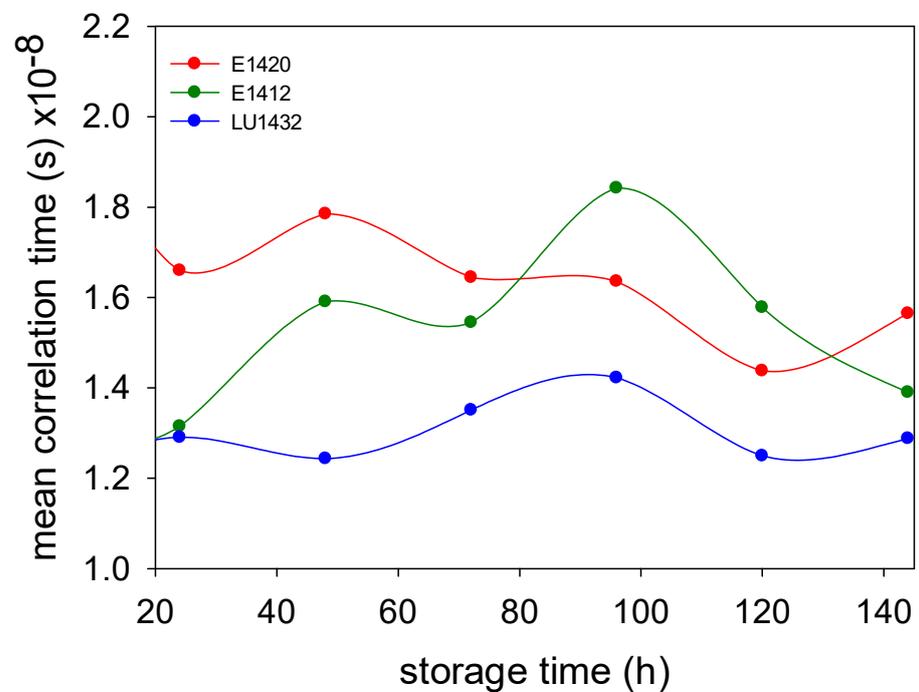


Figure 5. Time-dependent changes in mean values of proton motion correlation times of fat proton fraction in emulsions of bovine fat.

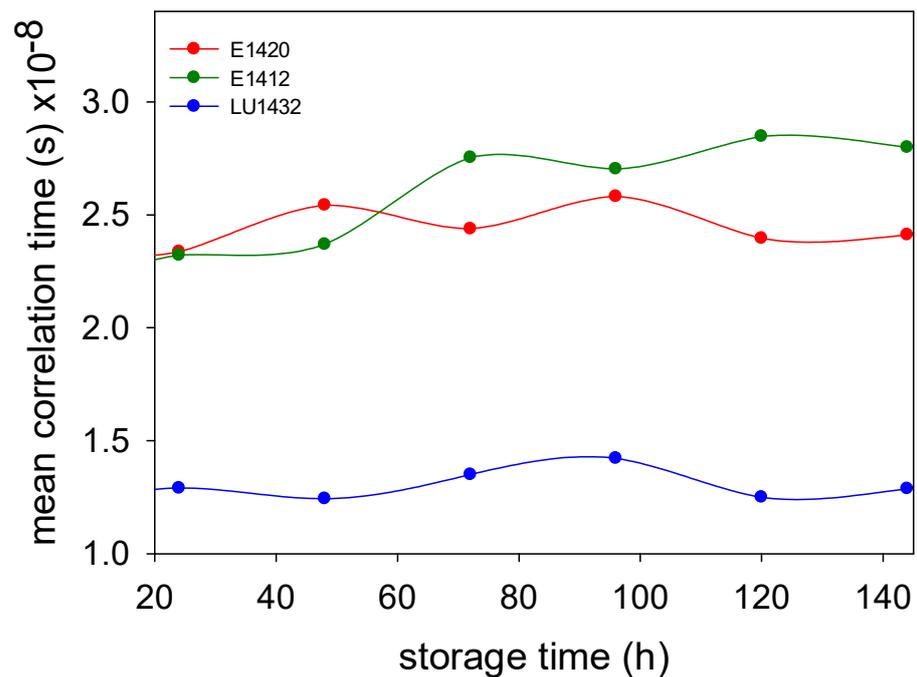


Figure 6. Time-dependent changes in mean values of proton motion correlation times of starch proton fraction in porcine fat emulsions emulsified with potato starches.

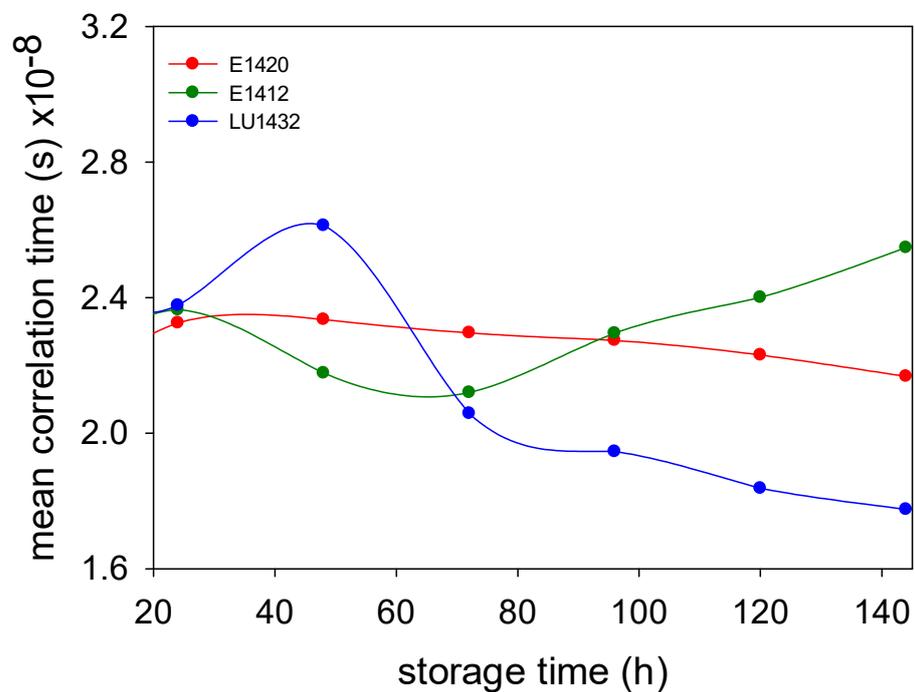


Figure 7. Time-dependent changes in mean values of proton motion correlation times of starch proton fraction in bovine fat emulsions emulsified with potato starches.

Analysis of animal fat emulsions stabilized with chemically modified starches (E 1420 and E 1412) showed that these emulsions are characterized by the relatively low dynamics of water molecules. This suggests a favorable, especially long-term, water binding in the presence of animal fats [47,48]. However, the results obtained suggest that the LU 1432 starch, which was only subjected to thermal treatment, does not fulfill the role of an emulsifier well. The water binding of physically modified starch is much weaker than that

of chemically modified starches [49]. Differences in time changes of the mean values of proton motion correlation times are observed depending on the type of fat used. Bovine fat emulsions can be successfully stabilized with E 1420 starch. On the other hand, porcine fat emulsions stabilized with E 1412 starch are characterized by better water binding. Thus, when using porcine fat in an emulsion, E 1412 starch can be recommended as an emulsifier or a substitute for porcine fat. In their research, Yang et al. [50] showed the beneficial effects of two different emulsifiers, so it can be assumed that it is also possible to obtain a synergistic effect when using different starches. Further research into the interactions of different starches could deepen our understanding of the mechanisms underlying emulsion formation and stabilization observed in current experiments.

4. Conclusions

To the best of our knowledge, this report is the first molecular-level description of the effect of the type of starch modification on the long-term stability of gels and emulsions obtained from animal fat. On the basis of the obtained results, it was found that chemically modified starch stabilizes the O/W emulsion significantly better than the physically modified starch. Nevertheless, depending on the type of fat, different modified starches appear to be more effective. For stabilizing the bovine-fat-based emulsions, smaller changes in stability were noted with starch E 1420, while the stabilizing effect in porcine-fat-based emulsions was stronger with E 1412.

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